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TITLE: THERMOSETTING RESIN COMPOSITION, CURING METHOD, WOODY MATERIAL AND MOLDED ARTICLE

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INVENTOR-INFORMATION:

NAME

HORIKI, SEINOSUKE  
KAJITA, TAKEHIKO  
ITO, KUNINORI

ASSIGNEE-INFORMATION:

NAME

NAGOYA YUKA KK

COUNTRY

N/A

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ABSTRACT:

PROBLEM TO BE SOLVED: To obtain the subject composition having long pot-life and excellent low-temperature curability and workability, giving a cured product having excellent strength, water resistance, oil resistance and weather resistance and useful as a molding material for building material, etc., by using a mixture of a specific curing agent and a precondensate of a phenolic compound and an aldehyde as a main component.

SOLUTION: This resin composition is composed mainly of a mixture of (A) a precondensate of a monohydric or a polyhydric phenol and an aldehyde (e.g. phenol-formaldehyde precondensate or phenol-resorcinol-formaldehyde precondensate) and (B) a uronic compound such as a compound of the formula (R is an alkylene or an arylene). Preferably, a sulfomethyl group or a sulfinethyl group is introduced into the component A.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the woody material and moldings using a thermosetting resin constituent useful in an application of the binder used in case the moldings of fiber, or a wood chip or inorganic powder is manufactured, a nonwoven fabric, a fiber knit fabric, paper, etc., an impregnant, or the adhesives of wood, its hardening technique, and this thermosetting resin constituent.

[0002]

[Description of the Prior Art] As an application of the water-soluble binder used in case the moldings of fiber, or a wood chip or inorganic powder is manufactured conventionally, a nonwoven fabric, a fiber knit fabric, paper, etc., an impregnant, or adhesives of wood, the initial condensate of a resol type phenolaldehyde system and the initial copolycondensation object of a phenol resorcinol aldehyde system are used.

[0003]

[Problem(s) to be Solved by the Invention] However, at a room temperature, since the above-mentioned initial condensate of a resol type phenolaldehyde system is unstable, it must be saved at low temperature, and it has a fault with the very short term which can be saved. And the 180-200-degree C heating at high temperature is usually required for the hardening, according to such a heating at high temperature, heat deterioration is produced in molding materials, such as fiber and a wood chip, and a heat energy cost also becomes high. In the case of 1 \*\* phenol, the polyhydric phenol, and an initial copolycondensation object of an aldehyde system like the initial copolycondensation object of a phenol resorcinol aldehyde system, when it is necessary to add an aldehyde and it uses formalin and an aldehyde like a paraformaldehyde as a curing agent as a curing agent in the case of use, since reactivity is too high, the pot life in the room temperature after curing agent addition is short, a working life is it 2 - 3 hours that it is long, and there is a fault that workability is very bad. Moreover, when hardening advanced considerably also in the phase of predrying after mixing this 1 \*\* phenol, a polyhydric phenol, and the initial copolycondensation object of an aldehyde system as a binder in using the hexamethylenetetramine of the pyrogenetic-reaction type instead of formalin and a paraformaldehyde as a curing agent, or carrying out application sinking in as an application or an impregnant, hardening advanced still quickly [ room temperature ] as for this predrying object, the moldability was lost and it could not save for a long period of time, there was a \*\*\*\* trouble. In order to improve the pot life after curing agent addition of a resorcinol system resin, amino resins, such as a methylolurea, a formaldehyde resin, a methylation methylolurea, a methylol melamine, a melamine formaldehyde resin, and a methylation methylol melamine, are added instead of an aldehyde as a curing agent, and the hardening technique which carries out heating hardening or more by pH seven is indicated (JP,57-053536,A). However, although the working life after curing agent addition was extended when this technique was applied to above-mentioned 1 \*\* phenol, polyhydric phenol, and initial copolycondensation object of an aldehyde system, heating of 180 degrees C or more was needed for hardening, and when the effect of hardening promotion of making heating into a low-temperature short time more was not expectable, the \*\*\*\* trouble had it.

[0004]

[Means for Solving the Problem] The moldings which used the hardening technique of the thermosetting resin constituent characterized by this invention making a principal component mixture of the initial condensate of 1 \*\* phenol and/or a polyhydric phenol, and an aldehyde and a \*\*\*\*\* system compound as a means for solving the above-mentioned conventional technical problem and this thermosetting resin constituent and this thermosetting resin constituent is offered.

[0005] this invention is explained in detail below. The thermosetting resin constituent of this invention makes a subject mixture of the initial copolycondensation object of 1 \*\* phenolaldehyde system, a polyhydric phenol and the initial copolycondensation object of an aldehyde system and/or 1 \*\* phenol, a polyhydric phenol and the initial copolycondensation object of an aldehyde system (initial copolycondensation object A of the following, and \*\*\*\*), and \*\*\*\*\* system compound B.

If 1 \*\* phenol used for initial copolycondensation object A of [\*\* 1 Phenol] this invention is illustrated Alkylphenols, such as a phenol, o-cresol, m-cresol, p-cresol, ethylphenol, iso-propyl phenol, a xylanol, 3, 5-xylanol, butylphenol, t-butylphenol, and a nonyl phenol, o-fluorophenol, m-fluorophenol, p-fluorophenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, o-\*\*\*\*\* phenol, m-\*\*\*\*\* phenol, p-\*\*\*\*\* phenol, o-iodine phenol, m-iodine phenol, p-iodine phenol, ortho aminophenol, m-aminophenol, para aminophenol, ortho nitrophenol, m-nitrophenol, p-nitrophenol, a 2, 4-dinitrophenol, 2, 4, They are

independent or two or more sorts of mixture of 1 \*\* phenols, such as 1 \*\* phenol substitution products, such as 6-trinitrophenol, and a naphthol.

[0006] If the polyhydric phenol used for initial copolycondensation object A of a [polyhydric-phenol] this invention is illustrated, they are independent or two or more sorts of mixture of polyhydric phenols, such as a resorcinol, an alkyl resorcinol, pyrogallol, a catechol, an alkyl catechol, hydroquinone, alkyl hydroquinone, a phloroglucine, a bisphenol, and dihydroxy naphthalene. A desirable thing is a resorcinol or an alkyl resorcinol among these polyhydric phenols, and especially a desirable thing is an alkyl resorcinol with the reaction rate quicker than a resorcinol with an aldehyde. As the above-mentioned alkyl resorcinol For example, 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, a 5-n-butyl resorcinol, 4, 5-dimethyl resorcinol, 2, 5-dimethyl resorcinol, 4, 5-diethyl resorcinol, 2, 5-diethyl resorcinol, 4, 5-dipropyl resorcinol, There are 2, 5-dipropyl resorcinol, a 4-methyl-5-ethyl resorcinol, a 2-methyl-5-ethyl resorcinol, a 2-methyl-5-propyl resorcinol, 2 and 4, a 5-trimethyl resorcinol, 2 and 4, a 5-triethyl resorcinol, etc. Since the polyhydric-phenol mixture obtained by dry distillation of the Estonia \*\* oil shale contains various reactant high alkyl resorcinols besides 5 \*\*\*\*\* resorcinol so much cheaply, it is the most desirable polyhydric-phenol raw material in this invention.

[0007] In order to manufacture initial copolycondensation object A of a [aldehyde and/or aldehyde donator] this invention, the above-mentioned 1 \*\* phenol and/or a polyhydric phenol, an aldehyde, and/or an aldehyde donator are condensed. The above-mentioned aldehyde donator means the compound which carries out generation supply of the aldehyde, if it decomposes. If the above-mentioned aldehyde and an aldehyde donator are illustrated, they are independent or two or more sorts of mixture, such as formalin, formaldehyde, a paraformaldehyde, a trioxane, an acetaldehyde, a propionaldehyde, a polyoxymethylene, a trichloroacetic aldehyde, a hexamethylenetetramine, a furfural, glyoxal, n-butylaldehyde, a caproaldehyde, an allyl-compound aldehyde, the Benz aldehyde, a crotonaldehyde, an acrolein, a tetrapod oxy-methylene, a phenylacetraldehyde, o-torr aldehyde, and a salicylaldehyde.

[0008] In a [condensation catalyst] this invention, in the case of condensation with 1 \*\* phenol and/or a polyhydric phenol, an aldehyde, and/or an aldehyde donator, if required, an acid or alkaline condensation catalyst will be added. Usually let the addition be an amount below 6 % of the weight (for it to only consider as % below) to 1 \*\* phenol and/or a polyhydric phenol. As the above-mentioned acid catalyst, for example A hydrochloric acid, a sulfuric acid, an orthophosphoric acid, a boric acid, oxalic acid, Formic acid, an acetic acid, a butyric acid, a benzenesulfonic acid, a phenolsulfonic acid, Para toluenesulfonic acid, Inorganic or organic acids, such as a naphthalene-alpha-sulfonic acid and a naphthalene-beta-sulfonic acid, Or acid anhydrides, such as ester of organic acids, such as oxalic acid dimethyl ester, and a maleic-acid anhydride, Manganese hydroxide, chromium hydroxide, an iron hydroxide, hydroxylation lead, copper hydroxide, zinc acetate, Formic-acid zinc, benzoic-acid zinc, a zinc chloride, ferric chloride, manganese acetate, a cadmium acetate, An ammonium chloride, an ammonium sulfate, an ammonium nitrate, an ammonium oxalate, An ammonium acetate, ammonium phosphate, an ammonium thiocyanate, An ammonium salt, monochloroacetic acid, and its specific salts, such as imido sulfonic-acid ammonium, There are urea adducts, such as a hydrochloride of aminess, such as organic halogenides, such as alpha and alpha' dichlorohydrin, a triethanolamine hydrochloride, and an aniline hydrochloride, a salicylic acid urea adduct, a stearin acid urea adduct, and an oenanthic-acid urea adduct, an N-trimethyl taurine, etc. As the above-mentioned alkaline catalyst, aminess, such as the weak-acid salts of alkali metal, such as the hydroxide of metals, such as a sodium hydroxide, a potassium hydroxide, a barium hydroxide, a calcium hydroxide, a calcium oxide, a barium oxide, a magnesium oxide, a zinc oxide, cobalt oxide, a lead oxide, nickel oxide, and an aluminum oxide, an oxide, a sodium carbonate, a sodium sulfite, sodium acetate, and a sodium phosphate, ammonia, a trimethylamine, a triethanolamine, a hexamethylenetetramine, and a pyridine, are illustrated, for example. You may use together the above-mentioned acidity or two or more sorts of alkaline catalysts.

[0009] Although the indifferent water is used as a solvent of initial copolycondensation object A in a [solvent] this invention If required, further A methanol, ethanol, an isopropanol, n-propanol, an isopropanol, n-butanol, an isobutanol, sec-butanol, t-butanol, n-amyl alcohol, isoamyl alcohol, n-hexanol, A methyl amyl alcohol, 2\*\*\*\*\* Norian, n-heptanol, n-octanol, trimethyl nonyl alcohol, a cyclohexanol, benzyl alcohol, furfuryl alcohol, a tetrahydrofurfuryl alcohol, loon ethyl alcohol, Alcohols, such as diacetone alcohol, An acetone, a methyl acetone, a methyl ethyl ketone, a methyl-n-propyl ketone, a methyl-n-butyl ketone, a methyl isobutyl ketone, a diethyl ketone, a G n-propyl ketone, a diisobutyl ketone, an acetonylacetone, a methyl oxide, a cyclohexanone, Ketones, such as a methylcyclohexanone, an acetophenone, and camphor Glycols, such as ethylene glycol, a diethylene glycol, a triethylene glycol, a propylene glycol, a trimethylene glycol, and a polyethylene glycol Glycol ethers, such as an ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, an ethylene glycol isopropyl ether, the diethylene-glycol monomethyl ether, and the triethylene-glycol monomethyl ether The ester, the derivatives of those of the above-mentioned glycols, such as an ethylene glycol diacetate and diethylene-glycol-monoethyl-ether acetate, The addition use of independent or two or more sorts of mixture of water fusibility organic solvents, such as ether, such as 1 and 4-dioxane, a diethyl cellosolve, a diethyl carbitol, ethyllactate, isopropyl lactate, a diethylene glycol diacetate, and a dimethylformamide, can be carried out. While an acetone etc. is a solvent, when using an alkyl resorcinol, it acts also as the complexing agent, and it brings a quieter reaction.

[0010] Without making the bottom of acidity or alkaline condensation catalyst presence, or a condensation catalyst exist, initial condensate A of a [initial condensate A] this invention is under heating, or in ordinary temperature, the condensation reaction of 1 \*\* phenol and/or a polyhydric phenol, an aldehyde, and/or the aldehyde donator is carried out, and they are obtained. The addition of the aldehyde in this case and/or an aldehyde donator is usually 0.2-3 mols to one mol of 1 \*\*

phenols, and is usually about 0.1-0.8 mols to a polyhydric phenol. When carrying out the copolycondensation of 1 \*\* phenol and the polyhydric phenol, it is desirable to usually carry out the copolycondensation of about 0.1-2 mols of the polyhydric phenols to one mol of 1 \*\* phenols. Or he has no presence of a catalyst. the copolycondensation of 1 \*\* phenol, a polyhydric phenol, an aldehyde, and/or the aldehyde donator is carried out -- making -- the bottom of presence of alkali or an acid catalyst -- How to condense simultaneously 1 \*\* phenol, a polyhydric phenol, an aldehyde, and/or an aldehyde donator, 1 \*\* phenol and/or the initial condensate of 1 \*\* phenolaldehyde -- a polyhydric phenol -- and -- or, although the technique of adding and carrying out the copolycondensation of an aldehyde and/or the aldehyde donator to a polyhydric phenol and the initial condensate of an aldehyde if required etc. is arbitration Desirable technique is made into the initial condensate of a resol type phenolaldehyde which condenses 1 \*\* phenol, an aldehyde, and/or an aldehyde donator under alkali catalyst presence, and has a methylol machine. Subsequently, a polyhydric phenol and/or a polyhydric phenol, and the initial condensate of an aldehyde system are added to this condensate, and if required, it is the technique of adding and carrying out the copolycondensation of an aldehyde and/or the aldehyde donator. A copolycondensation is carried out to one mol of 1 \*\* phenols in this case at a rate of 0.2-6.0 mols of aldehydes, and 0.1-2.0 mols of polyhydric phenols. Although the aqueous solution of initial condensate A is usually stable in the with a pH of eight to nine or more alkalinity side here, it is unstable at a neutrality or acidity side, and the problem which causes a layer separation arises. It is desirable to introduce a sulfo methyl group and/or a \*\*\*\*\* methyl group into this first time condensate A, for solving this trouble. The water solubility in large pH field reached [ from the alkalinity of this first time condensate A ] acid is remarkably improved by introduction of the above-mentioned sulfo methyl group and/or a \*\*\*\*\* methyl group, and the thermosetting resin constituent of a stable this invention is obtained.

[0011] As a third component of the above-mentioned initial condensate A a request -- if -- a urea, a melamine, thiourea, benzoguanamine, toluene, a xylene, a cumarone, a cyclohexanone, cashew oil, tannin, \*\*\*\*\* a shellac, rosin or a rosin derivative, a petroleum resin, a methanol, ethanol, and an isopropanol -- n-butanol, an isobutanol, ethylene glycol, a diethylene glycol, a polyethylene glycol, a glycerol, furfuryl alcohol, the linseed oil, tung oil, castor oil, Kinds, such as an acetone and a methyl ethyl ketone, or two sorts or more are made into a copolycondensation agent, a modifier, or a complexing agent, and even if it adds and it denaturalizes a copolycondensation or by mixing among a reaction or after a reaction end at the time of reaction start of condensation or a copolycondensation, it does not interfere.

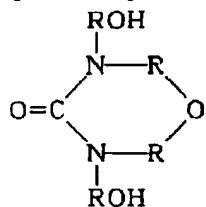
[0012] With the sulfo methylation object of initial condensate A of a phenolaldehyde system of a [sulfo methylation object and \*\*\*\*\* methylation object] this invention, and a \*\*\*\*\* methylation object When making 1 \*\* phenol and/or a polyhydric phenol, an aldehyde, and/or an aldehyde donator condense, It is \*\*\*\*\* about the initial condensate of sulfo methylation, the initial copolycondensation object, the initial condensate of \*\*\*\*\* methylation, or initial copolycondensation object which carries out the addition reaction of the \*\* which also spreads a sulfo methylation agent and/after a reaction end in the middle of the time of this condensation-reaction start, or a reaction, and is obtained [ \*\* ] in a \*\*\*\*\* methylation agent. since it is desirable to add in case 1 \*\* phenol, an aldehyde, and/or an aldehyde donator are condensed under alkali catalyst presence and it considers as the initial condensate of a phenolaldehyde system as for a sulfo methylation agent or a \*\*\*\*\* methylation agent and 1 \*\* phenol is beforehand sulfo-methylated and/or \*\*\*\*\* methylated in this case -- an aldehyde and/or an aldehyde donator, and condensation -- or even if it carries out a copolycondensation, it does not interfere If the above-mentioned initial condensate A is sulfo-methylated and/or \*\*\*\*\* methylated, the working life at the time of the reaction activity with the aldehyde of this first time condensate A falling, and adding an aldehyde and/or an aldehyde donator as a curing agent will be extended. Moreover, since the reaction activity with the aldehyde of this copolycondensation object will fall most if pH is kept general into fine acidity from neutrality although the water solubility of this first time condensate A increases and good water solubility comes to be shown in large pH field by the side of neutrality or acidity by introduction of a sulfo methyl group and/or a \*\*\*\*\* methyl group, a working life becomes the longest. Since there is a possibility that hardening may be too slow even if it adds the \*\*\*\*\* compound which a fall of the reaction activity with an aldehyde may be remarkable, and carries out a postscript according to sulfo methylation and/or \*\*\*\*\* methylation, when initial condensate A is the initial condensate of 1 \*\* phenol, it is desirable to choose 1 \*\* phenol, a polyhydric phenol, and the initial copolycondensation object of an aldehyde system as initial condensate A in this invention. As for sulfo methylation, it is desirable to make a sulfo methyl group into the domain of 0.05-0.5 mols to one mol of 1 \*\* phenols. When a sulfo methyl group is 0.05 mols or less, a fall of the reaction activity with an aldehyde is inadequate, and short \*\* past \*\*\*\*\* has a working life. Moreover, if a sulfo methyl group is 0.5 mols or more, the reaction activity with an aldehyde will fall too much, the hardened material which has sufficient intensity by heating of 120-140 degrees C or less is not obtained, and the fault that the durability of a hardened material is bad arises. It is desirable also in \*\*\*\*\* methylation, to make a \*\*\*\*\* methyl group into the domain of 0.05-0.5 mols to the monohydric phenol of one mol, since it is the same as that of the case of sulfo methylation. If initial condensate A is sulfo-methylated and/or \*\*\*\*\* methylated, the stable mixed constituent with a \*\*\*\*\* system compound will be obtained also neutrality and under acid. That is, in pH field to which the reaction activity of a \*\*\*\*\* system compound becomes higher, this mixed constituent can be used and low temperature and the advantage which may advance a hardening reaction by short-time heating arise more.

[0013] As a sulfo methylation agent used in a [sulfo methylation agent and \*\*\*\*\* methylation agent] this invention, hydroxy alkane sulfonic acids, such as a water-soluble sulfite with quaternary amines, such as a sulfurous acid, a pile sulfurous acid or a meta-pile sulfurous acid, alkali metal or a trimethylamine, and benzyl trimethylammonium, or the fourth class ammonium and hydroxy methanesulfon acid chloride obtained by the reaction of these water-soluble sulfites and

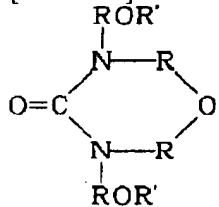
aldehydes, are illustrated. As a \* system compound B of this invention, alkyl sulfoxylate, such as the sodium hydrosulfites of alkali metal, such as aliphatic series, such as sodium formaldehyde sulfoxylate (Rongalite) and benzaldehyde sodium \* system compound B, alkali-metal sulfoxylate of an aromatic aldehyde, a sodium sodium hydrosulfite, and magnesium hydro \* system compound B, and an alkaline earth metals and sodium ethyl sulfoxylate, is illustrated. Since a sulfo methylation reaction advances in parallel to a \* system compound B of this invention when using a \*\* 2 thionic-acid alkali-metal salt as a \* system compound B, a sulfo methylation object generates with a \* system compound B of this invention.

[0014] In the thermosetting resin constituent of a [ \* system compound B] this invention, \* system compound B is added by this first time condensate A as a curing agent. The above-mentioned \* system compound B is a resultant with a urea and/or thiourea, an aldehyde, and/or an aldehyde donator, and it usually has the structure expression of the following-izing 1. It is dependent on the modality of raw material aldehyde which R is an alkyl group or an aryl group, and is used here. Furthermore, alkoxy \*\* of the ROH base may be carried out like the structure expression of the following-izing 2 or \*\* 3. R' is an alkyl group or an aryl group here.

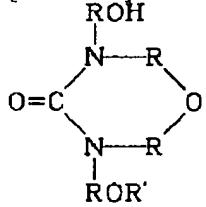
[Formula 1]



[Formula 2]



[Formula 3]



The typical example of \* system compound B of this invention is uronic dimethylol which is a resultant (one mol of ureas, and four mols of formaldehyde), and the dimethoxy-ized product is raised further. Although it is comparatively stable, if it heats at some dozens of degrees C or more, an activation will be started, in ordinary temperature, if this is further performed under acid, it will activate much more actively, and \* system compound B acts as a curing agent to the initial condensate of a phenolaldehyde system. And the activity to the hardening reaction has the property that it is more remarkable than different wave node ring compounds, such as \* system compound B which has other \* system compound B of roll machines, an ethylene urea, a propylene urea, and a \* system compound B, or a methylolurea, a formaldehyde resin, a methylol melamine, a melamine formaldehyde resin, etc., and is high. Therefore, a \* system compound B serves as the very effective curing agent which carries out heating hardening of the initial condensate of a phenolaldehyde system in a low-temperature short time.

[0015]

[Curing catalyst] It does not interfere, even if it adds a still acid or alkaline compound as a curing catalyst in the case of hardening to the thermosetting resin constituent of this invention which consists of initial condensate A and \* system compound B into which the sulfo methyl group and/or the \* system compound B methyl group are introduced in addition to the above-mentioned \* system compound B. If the above-mentioned acid curing catalyst is illustrated, a hydrochloric acid, a sulfuric acid, a nitric acid, a phosphoric acid, a pyrophosphoric acid, Polyphosphoric acid, a sulfonic acid, a hydrobromic acid, a hydroiodic acid, trichloroacetic acid, A benzenesulfonic acid, a chlorosulfonic acid, Para toluenesulfonic acid, A phenolsulfonic acid, ethane sulfonic acid, a mixed alkane sulfonic acid, A meta-benzene disulfon acid, a naphthalene alpha-sulfonic acid, a 1-naphthol-8-sulfonic acid, A meta-xylene sulfonic acid, a xylene sulfonic acid, a polymeric sulfonic acid, A styrene sulfonic acid, an anthraquinone-2-sulfonic acid, anthraquinone-2 and 7-disulfon acid,

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